

Interacting pairs in natural orbital functional theory

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Outline

- 1 Introduction to the Natural Orbital Functional Theory (NOFT)
- 2 The intrapair electron correlation
 - an independent pair model: PNOF5
- 3 The interpair electron correlation
 - an interacting pair model: PNOF6
- 4 Closing Remarks

The exact energy functional

Consider an N-electron molecule described by a non-degenerate state Ψ .

\hat{H} has only one- and two-particle operators, so the electronic energy in the BO approximation is an explicitly known functional of the spinless 1- and 2-RDMs:

$$E[N, \Gamma, D] = -\frac{1}{2} \int \nabla_1^2 \Gamma(\mathbf{r}'_1, \mathbf{r}_1) |_{\mathbf{r}'_1=\mathbf{r}_1} d\mathbf{r}_1 + \int \Gamma(\mathbf{r}_1, \mathbf{r}_1) v(\mathbf{r}_1) d\mathbf{r}_1 \\ + \int \frac{D(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1, \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2$$

$$\Gamma(\mathbf{r}'_1, \mathbf{r}_1) = N \sum_{\sigma_1} \int \Psi^*(\mathbf{r}'_1, \sigma_1, \mathbf{x}_2, \dots, \mathbf{x}_N) \Psi(\mathbf{r}_1, \sigma_1, \mathbf{x}_2, \dots, \mathbf{x}_N) d\mathbf{x}_2 \dots d\mathbf{x}_N$$

$$D(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1, \mathbf{r}_2) = \frac{N(N-1)}{2} \sum_{\sigma_1, \sigma_2} \int |\Psi(\mathbf{r}_1, \sigma_1, \mathbf{r}_2, \sigma_2, \mathbf{x}_3, \dots, \mathbf{x}_N)|^2 d\mathbf{x}_3 \dots d\mathbf{x}_N$$

$$\Gamma(\mathbf{x}'_1, \mathbf{x}_1) = \frac{2}{N-1} \int D(\mathbf{x}'_1, \mathbf{x}_2; \mathbf{x}_1, \mathbf{x}_2) d\mathbf{x}_2 \quad \Rightarrow \quad E[N, \Gamma, D] = E[N, D]$$

The variational approach in quantum chemistry

- The wavefunction theories (CI, CC, ...)

- Fundamental Variable: $\Psi(\mathbf{x}_1, \dots, \mathbf{x}_N) \Rightarrow D_\Psi$ (by contraction)

- The ground-state energy: $E_0 = \inf_{\Psi \in \mathcal{L}_N} E[\Psi] = E[\Psi_0] \equiv E[N, D_{\Psi_0}]$

- The variational theories without wavefunction

Method :	DFT	1DMFT		2DMFT
Variable :	$\rho_\Psi(\mathbf{r})$	$\Gamma_\Psi(\mathbf{x}'_1, \mathbf{x}_1)$		$D_\Psi(\mathbf{x}'_1, \mathbf{x}'_2; \mathbf{x}_1, \mathbf{x}_2)$
			(reconstruction)	
Functional :	$E_\Psi[N, \rho_\Psi]$	$E_\Psi[N, \Gamma_\Psi]$	\implies	$E[N, D_\Psi]$
	(HK)	(Gilbert)		(exact)

The N-representability Problem in DFT and 1DMT

- ① The N-representability of $\rho(\Gamma)$: $\rho_{\Psi}(\Gamma_{\Psi}), \Psi \Leftrightarrow \rho(\Gamma)$

- the necessary and sufficient conditions are known

- DFT: $\rho \geq 0, \int \rho(\mathbf{r}) d\mathbf{r} = N$
- 1DMFT: $0 \leq \Gamma \leq ql, \text{Tr}(\Gamma) = N$

- ② The functional N-representability: $E_{\Psi}[N, \rho_{\Psi}] (E_{\Psi}[N, \Gamma_{\Psi}])$

$$E[\Psi] = E[D_{\Psi}] \Leftrightarrow E[\rho_{\Psi}] (E[\Gamma_{\Psi}])$$

- some practical necessary conditions known for the 2-RDM

$$D \geq 0, Q \geq 0, G \geq 0$$

Natural Orbitals and Occupation Numbers

The 1-RDM can be diagonalized by a unitary transformation of the spin-orbitals $\{\phi_i(\mathbf{x})\}$:

$$\Gamma_{ki} = n_i \delta_{ki}, \quad \Gamma(\mathbf{x}'_1, \mathbf{x}_1) = \sum_i n_i \phi_i(\mathbf{x}'_1) \phi_i^*(\mathbf{x}_1)$$

$\phi_i(\mathbf{x})$: natural spin-orbital

n_i : occupation number

- $E_\Psi[N, \Gamma_\Psi] \Rightarrow E_\Psi[N, \{n_i, \phi_i\}]$
- necessary and sufficient conditions for N-representability of Γ :

$$0 \leq n_i \leq 1, \quad \sum_i n_i = N$$

The electronic energy in NOFT

The energy $E[N, \Gamma, D]$ is expressed in terms of the diagonal 1-RDM:

$$E[N, \{n_i, \phi_i\}] = \sum_i n_i \mathcal{H}_{ii} + \sum_{ijkl} D[n_i, n_j, n_k, n_l] \langle kl | ij \rangle$$

- \mathcal{H}_{ii} : core-Hamiltonian
- $\{n_i\}$: occupation numbers
- $\langle kl | ij \rangle$: 2e- integrals
- $\{\phi_i(\mathbf{x})\}$: natural orbitals

2-RDM: $D[n_i, n_j, n_k, n_l] \Leftarrow$ reconstruction functional

Advantage of NOFT with respect to DFT

the kinetic energy is explicitly defined and
does not require the construction of a functional

1. introduction to the NOF theory
2. the intrapair electron correlation
3. the interpair electron correlation

the energy functionals, the N-representability,
 the natural orbital functional
 the reconstruction functional (bottom-up method)

Cumulant expansion of the 2-RDM

$$D_{pq,rt}^{\sigma\sigma,\sigma\sigma} = \frac{n_p^\sigma n_q^\sigma}{2} (\delta_{pr}\delta_{qt} - \delta_{pt}\delta_{qr}) + \lambda_{pq,rt}^{\sigma\sigma,\sigma\sigma} \quad (\sigma = \alpha, \beta)$$

$$D_{pq,rt}^{\alpha\beta,\alpha\beta} = \frac{n_p^\alpha n_q^\beta}{2} \delta_{pr}\delta_{qt} + \lambda_{pq,rt}^{\alpha\beta,\alpha\beta}$$

$$\lambda_{pq,rt}^{\sigma\sigma,\sigma\sigma} = -\frac{\Delta_{pq}^{\sigma\sigma}}{2} (\delta_{pr}\delta_{qt} - \delta_{pt}\delta_{qr}), \quad \lambda_{pq,rt}^{\alpha\beta,\alpha\beta} = -\frac{\Delta_{pq}^{\alpha\beta}}{2} \delta_{pr}\delta_{qt} + \frac{\Pi_{pr}}{2} \delta_{pq}\delta_{rt}$$

Int. J. Quantum Chem. 106, 1093 (2006)

Δ : real symmetric matrix ($\Delta_{pq}^{\sigma_1\sigma_2} = \Delta_{qp}^{\sigma_2\sigma_1}$)

Sum Rules: $\sum_{q \neq p} \Delta_{pq}^{\sigma\sigma} = n_p^\sigma (1 - n_p^\sigma)$, $\sum_q \Delta_{pq}^{\alpha\beta} = \Pi_{pp}$

Π : spin-independent Hermitian matrix

($\Pi_{pr}^{\alpha\alpha} = \Pi_{pr}^{\alpha\beta} = \Pi_{pr}^{\beta\alpha} = \Pi_{pr}^{\beta\beta} = \Pi_{pr}$, $\Pi_{pr} = \Pi_{rp}^*$)

Singlets: $|SM_S\rangle = |00\rangle$

1 spin-restricted formalism:

- $|\phi_i\rangle = |\varphi_p\rangle \otimes |\sigma\rangle$, $\varphi_p(\mathbf{r}) = \varphi_p^\alpha(\mathbf{r}) = \varphi_p^\beta(\mathbf{r})$

- $n_p^\alpha = n_p^\beta = n_p$, $2 \sum_p n_p = N$

- $\Delta_{pq}^{\alpha\alpha} = \Delta_{pq}^{\alpha\beta} = \Delta_{pq}^{\beta\alpha} = \Delta_{pq}^{\beta\beta} = \Delta_{pq}$

2 $\langle \widehat{S}^2 \rangle = 0 \Rightarrow \Delta_{pp} = n_p^2$, $\Pi_{pp} = n_p$ (J. Chem. Phys. 131, 021102, 2009).

$$\Delta_{pq} = n_p^2 \delta_{pq} + \Delta(n_p, n_q)(1 - \delta_{pq}), \quad \sum_q \Delta_{pq} = n_p$$

$$\Pi_{pq} = n_p \delta_{pq} + \Pi(n_p, n_q)(1 - \delta_{pq})$$

The N-representability and off-diagonal elements

- ① Analytic constraints imposed by necessary positivity conditions of the 2-matrix N-representability

- $D \geq 0, Q \geq 0$

$$\Delta(n_p, n_q) \leq n_p n_q, \quad \Delta(n_p, n_q) \leq h_p h_q \quad (h_p = 1 - n_p)$$

- $G \geq 0$

$$\Pi^2(n_p, n_q) \leq [n_p h_q + \Delta(n_p, n_q)] [h_p n_q + \Delta(n_p, n_q)]$$

- ② PNOF:

$$E = \sum_p n_p (2\mathcal{H}_{pp} + \mathcal{J}_{pp}) + \sum'_{pq} [n_q n_p - \Delta(n_q, n_p)] (2\mathcal{J}_{pq} - \mathcal{K}_{pq}) + \sum'_{pq} \Pi(n_q, n_p) \mathcal{L}_{pq}$$

Off-diagonal elements of Δ - and Π -matrices ($p \neq q$)PNOF5 (n_c): $g = 1, \dots, F$ ($F = N/2$)

$$\Delta^g(n_p, n_q) = n_p n_q \delta_{p\Omega_g} \delta_{q\Omega_g}, \quad \delta_{p\Omega_g} = \begin{cases} 1, & p \in \Omega_g \\ 0, & p \notin \Omega_g \end{cases}$$

$$\Pi^g(n_p, n_q) = \delta_{p\Omega_g} \delta_{q\Omega_g} \begin{cases} -\sqrt{n_p n_q}, & p=g \text{ or } q=g \\ \sqrt{n_p n_q}, & p, q > F \end{cases}$$

- Ω_g is a subspace containing an orbital g below the Fermi level ($g \leq F$), and n_c orbitals with $p > F$.
- subspaces are mutually disjoint: $\Omega_{g1} \cap \Omega_{g2} = \emptyset$
- sum rule: $\sum_{q \in \Omega_g} n_q = 1$ ($g = 1, \dots, F$)

1. introduction to the NOF theory
2. the intrapair electron correlation
3. the interpair electron correlation

the independent pair model: PNOF5 (n_c)
diradicals, homolytic dissociations
A generating wavefunction of PNOF5e

The energy functional for PNOF5e (real orbitals)

$$E = \sum_{g=1}^F E_g + \sum_{f \neq g}^F \sum_{p \in \Omega_f} \sum_{q \in \Omega_g} n_p n_q (2\mathcal{J}_{qp} - \mathcal{K}_{qp})$$

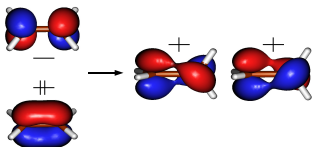
$$E_g = \sum_{p \in \Omega_g} n_p (2\mathcal{H}_{pp} + \mathcal{J}_{pp}) + \sum_{p \neq q} \Pi^g(n_p, n_q) \mathcal{K}_{qp}$$

$$\Pi^g(n_p, n_q) = \delta_{p\Omega_g} \delta_{q\Omega_g} \begin{cases} -\sqrt{n_p n_q}, & p=g \text{ or } q=g \\ \sqrt{n_p n_q}, & p, q > F=N/2 \end{cases}$$

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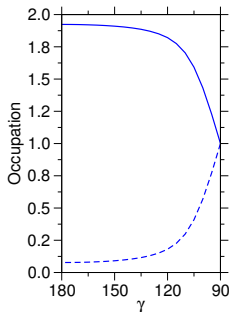
Ethylene Torsion (cc-pVDZ)



Natural Orbital Functional Theory correctly describes degeneracy effects in diradical reactions

	ΔE (kcal/mol)
CASPT2(12,12)	65.5
PNOF5	65.6
B3LYP [‡]	63.8
PBE0 [‡]	60.9
M06-2X [‡]	66.9

[‡] Broken symmetry energies for TS. $\langle S^2 \rangle = 1.01$

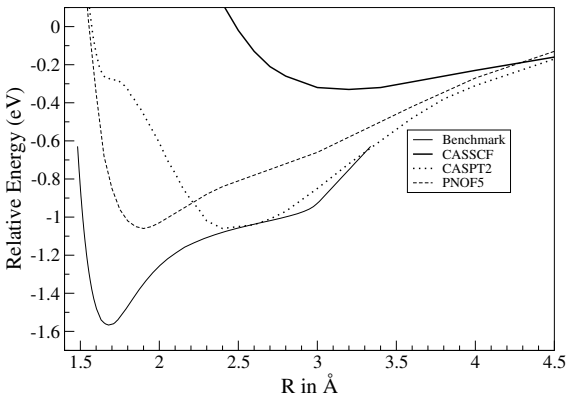


J. Chem. Phys. 134, 164102, 2011

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Dissociation of transition metal dimers (Cr_2)



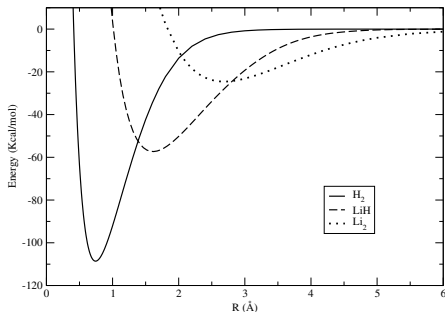
(14s11p6d3f)/[8s6p4d1f] basis set

Phys. Chem.. Chem. Phys. 15, 2055, 2013

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Dissociation curves for H_2 , LiH and Li_2 (aug-cc-pVTZ)



Errors in total energies (kcal/mol)

	PNOF5e	CCSD(T)* (E_h)
H_2	0.0	-1.172756
LiH	2.3	-8.048590
Li_2	4.8	-14.954066

* reference values at the equilibrium

	PNOF5e ($n_c > 1$)					Exp.				
	R_e	D_e	ω_e	$\omega_e x_e$	$\omega_e y_e$	R_e	D_e	ω_e	$\omega_e x_e$	$\omega_e y_e$
H_2	0.743	108.6	4395.0	121.6	0.8	0.743	109.5	4401.2	121.3	0.8
LiH	1.613	57.3	1382.3	21.7	0.2	1.595	58.0	1405.5	23.2	0.2
Li_2	2.692	24.6	348.5	3.9	0.1	2.673	24.4	351.4	2.6	0.0

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APSG generating wavefunction of PNOF5e

$$|0\rangle = |\Phi_0\rangle + |\Phi_d\rangle + |\Phi_q\rangle + \dots + |\Phi_F\rangle, \quad F = N/2$$

$$|\Phi_0\rangle = d_0 |\Psi_{HF}\rangle \qquad |\Phi_d\rangle = - \sum_{g=1}^F \sum_{p \in \Omega'_g} d_g^p |\Psi_{g\bar{g}}^{p\bar{p}}\rangle$$

$$|\Phi_q\rangle = \sum_{g < f}^F \sum_{p \in \Omega'_g} \sum_{q \in \Omega'_f} d_{gf}^{pq} |\Psi_{g\bar{g}f\bar{f}}^{p\bar{p}q\bar{q}}\rangle$$

...

$$|\Phi_{N/2}\rangle = (-1)^F \sum_{p \in \Omega'_1} \sum_{q \in \Omega'_2} \dots \sum_{r \in \Omega'_F} d_{12\dots F}^{pq\dots r} |\Psi_{1\bar{1}2\bar{2}\dots F\bar{F}}^{p\bar{p}q\bar{q}\dots r\bar{r}}\rangle$$

$$d_0 = \sqrt{n_1 n_2 \dots n_F}, \quad d_g^p = d_0 \sqrt{\frac{n_p}{n_g}}, \quad d_{gf}^{pq} = d_0 \sqrt{\frac{n_p n_q}{n_g n_f}}, \quad \dots$$

J. Chem. Phys. 139, 064111, 2013

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PNOF6. Miroslav P. Huzar
 Electron Delocalization: D_{2h} H_4
 Electron Delocalization: Benzene.

Off-diagonal elements of Δ - and Π -matrices for PNOF6

$$\Delta_{qp} = \begin{cases} e^{-2S} h_q h_p \\ \frac{\gamma_q \gamma_p}{S_\gamma} \\ e^{-2S} n_q n_p \end{cases} \quad \Pi_{qp} = \begin{cases} -e^{-S} (h_q h_p)^{1/2} & q \leq F, p \leq F \\ -\Pi_{qp}^\gamma & q \leq F, p > F \\ -\Pi_{qp}^\gamma & q > F, p \leq F \\ e^{-S} (n_q n_p)^{1/2} & q > F, p > F \end{cases}$$

$$S = \sum_{q=1}^F h_q = \sum_{q=F+1}^N n_q, \quad S_\gamma = \sum_{q=1}^F \gamma_q = \sum_{q=F+1}^N \gamma_q, \quad S_\alpha = \sum_{q=1}^F \alpha_q = \sum_{q=F+1}^N \alpha_q$$

$$\gamma_p = n_p h_p + \alpha_p^2 - \alpha_p S_\alpha, \quad \alpha_p = \begin{cases} e^{-S} h_p, & 1 \leq p \leq F \\ e^{-S} n_p, & F < p \leq N \end{cases}$$

$$\Pi_{qp}^\gamma = \left(n_q h_p + \frac{\gamma_q \gamma_p}{S_\gamma} \right)^{1/2} \left(h_q n_p + \frac{\gamma_q \gamma_p}{S_\gamma} \right)^{1/2}$$

J. Chem. Phys. 141, 044107, 2014



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PNOF6. Homolytic dissociations.
 Electron Delocalization: D_{2h} H_4
 Electron Delocalization: Benzene.

PNOF6: A natural orbital JKL-functional

$$E = \sum_{g=1}^F E_g + \sum_{f \neq g}^F (E_{fg}^{in} + E_{fg}^{out}) + 2 \sum_{p=F+1}^N \sum_{q=1, \neq \tilde{p}}^F E_{pq}^\gamma$$

$$E_g = \sum_{p \in \Omega_g} n_p (2\mathcal{H}_{pp} + \mathcal{J}_{pp}) + 2E_{g\tilde{g}}^\gamma$$

$$E_{fg}^{in} = (n_f n_g - e^{-2S} h_f h_g) (2\mathcal{J}_{gf} - \mathcal{K}_{gf}) - e^{-S} \sqrt{h_f h_g} \mathcal{L}_{gf}$$

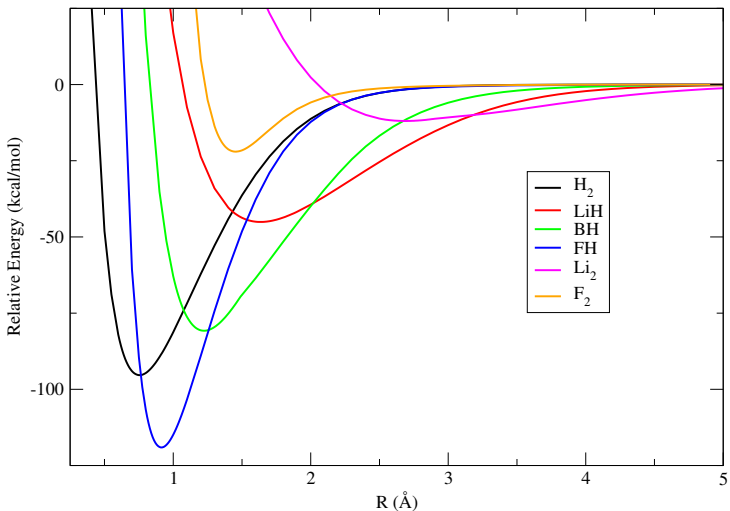
$$E_{fg}^{out} = (1 - e^{-2S}) n_{\tilde{f}} n_{\tilde{g}} (2\mathcal{J}_{\tilde{g}\tilde{f}} - \mathcal{K}_{\tilde{g}\tilde{f}}) + e^{-S} \sqrt{n_{\tilde{f}} n_{\tilde{g}}} \mathcal{L}_{\tilde{g}\tilde{f}}$$

$$E_{pq}^\gamma = \left(n_q n_p - \frac{\gamma_q \gamma_p}{S_\gamma} \right) (2\mathcal{J}_{pq} - \mathcal{K}_{pq}) - \Pi_{qp}^\gamma \mathcal{L}_{pq}$$

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PNOF6. Homolytic dissociations.
Electron Delocalization: D_{2h} H_4
Electron Delocalization: Benzene.

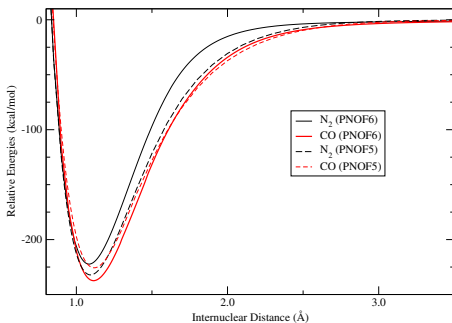
Homolytic dissociations / PNOF6 / cc-pVTZ



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Homolytic dissociations of CO and N_2 / cc-pVTZ

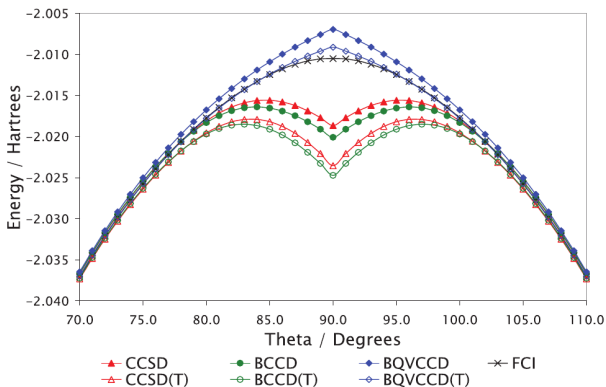
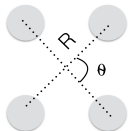


	PNOF5			PNOF6			Experimental		
	R_e	μ	D_e	R_e	μ	D_e	R_e	μ	D_e
N_2	1.090	0.00	239.3	1.084	0.00	222.3	1.098	0.00	228.3
CO	1.116	0.22	225.6	1.114	0.10	237.4	1.128	0.11	259.3

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D_{2h} H_4 Model / CC, FCI / aug-cc-pVDZ / $R = 1.75 \text{ \AA}$



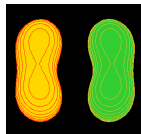
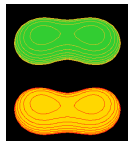
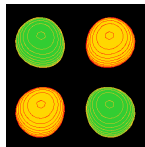
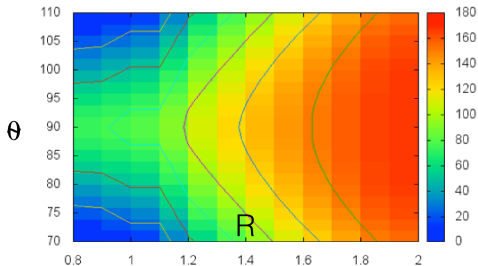
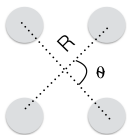
J. B. Robinson and P. J. Knowles, J. Chem. Phys. 137, 054301, 2012

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D_{2h} H_4 Model / PNOF6 / aug-cc-pVDZ

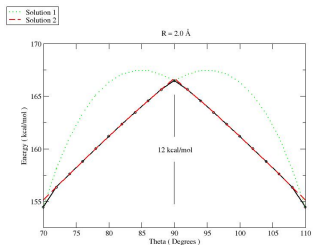
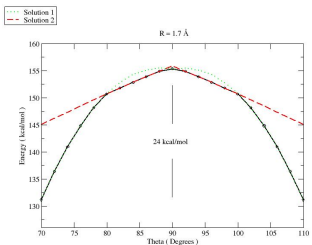
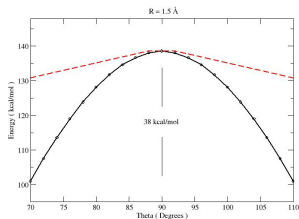
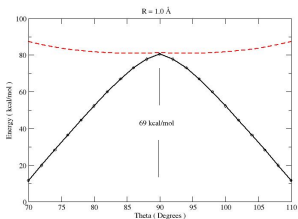
Orbitals ($\theta = 90^\circ$)



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PNOF6. Homolytic dissociations.
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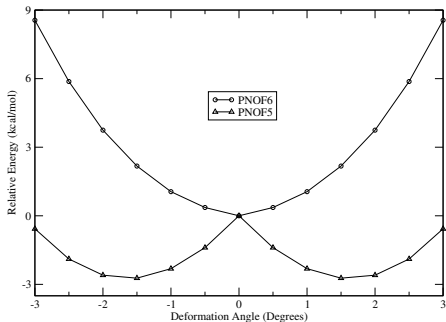
D_{2h} H_4 Model / PNOF6 / $R = 1.0, 1.5, 1.7, 2.0 \text{ \AA}$



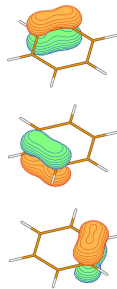
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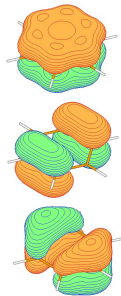
Potential energy curve for the distortion of benzene



PNOF5



PNOF6



The three bonding π orbitals

Closing remarks

- Two natural orbital functionals have been analyzed
PNOF5: Independent pairs PNOF6: Interacting pairs
- The new functional PNOF6 seems to describe in a more balanced way the static (non-dynamic) and dynamic correlations.
- More dynamic correlation has to be incorporated for improving the results

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Acknowledgements

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Thank you for your attention !!!